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DETERMINATION OF TRIVALENT CHROMIUM IN CHROMIUM PLATING SOLUTIONS USING A REDOX TITRATION AND INDICATOR

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13. ABSTRACT *(Maximum 200 words)*

The chemical literature lacks a simple non-instrumental analytical method to determine and adequately monitor trivalent chromium in chromium plating solutions during the chromium plating process. In this report, a simple method for analyzing and monitoring trivalent chromium during the chromium plating process is presented. The optimum operating range of trivalent chromium is 0 to 7.5 g/l, and the resulting precisions are in the 0 to 1.5-g/l range, providing adequate monitoring of these plating solutions supported by five years of testing.

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INTRODUCTION

The chemical literature lacks a simple non-instrumental analytical method to determine and adequately monitor trivalent chromium in chromium plating solutions during the chromium plating process. Lack of optimization of these plating solutions causes serious problems for the chromium plating industry such as poor quality products, wasted human resources, and wasted electrical energy.

A common chemical analysis method to determine chromium in chromium plating solutions uses atomic absorption or inductively coupled plasma spectrometry (ref 1). However, the problem with this method is that hexavalent chromium ions are also present and must be corrected by a separate analytical method to determine trivalent chromium. Relative precisions of the combined methods are in the 3 to 5-percent range.

Another chemical analysis method to determine trivalent chromium in chromium plating solutions is by sodium thiosulfate titration using a potassium iodide/starch indicator (refs 2-5). This method determines hexavalent chromium, but if trivalent chromium is subsequently oxidized, then it will also determine the total chromium with the difference representing trivalent chromium. This method is time-consuming, since the sodium thiosulfate is unstable and must be standardized every time it is used, although after standardization, relative precisions are in the 1 to 2-percent range.

The simple method given here provides acceptable analysis and monitoring of trivalent chromium in chromium plating solutions. The method uses a ferrous ammonium sulfate redox titrant and redox indicator. It also determines hexavalent chromium, but if trivalent chromium is subsequently oxidized, then it will also determine the total chromium with the difference representing trivalent chromium. General background information on redox titration is extensive (refs 2-6).

EXPERIMENTAL PROCEDURE

Strict analytical chemistry methods and procedures are followed throughout this experimental section. An excellent source of reference for these methods and procedures is by Fritz and Schenk (ref 6).

One analytical reagent grade standard solution is required. This solution is a 4.90 ± 0.01-g/l potassium dichromate solution that meets American Chemical Society (ACS) Standards and Federal Specification O-C-303D for hexavalent chromium (refs 7,8).

Three other reagent grade solutions are required. The first is the redox titrant which has 45.0 ± 0.01 grams of ferrous ammonium sulfate (six hydrate) and 60 ± 1 milliliters (ml) of sulfuric acid per liter of total solution. The second is the redox indicator which is a 10.0 ± 0.1-g/l sodium diphenylamine sulfonate solution. The third is a complexing agent which is a 1.70 ± 0.05-g/l silver nitrate solution.

Preparation of a potassium dichromate standard for redox titration analysis requires that 25 ml of the analytical reagent grade standard solution prepared above is diluted to about the 200-ml mark with deionized water in a 400-ml beaker. In addition, 5 ml of concentrated sulfuric acid, 5 ml of concentrated phosphoric acid, a stirring bar, and five drops of the redox indicator are added to the beaker. The redox titrant is titrated to a green endpoint recording the amount of titrant dispensed.

Preparation of a chromium plating sample solution for hexavalent chromium analysis by redox titration requires that 10 ml of sample solution is pipetted into a 500-ml volumetric flask which is filled to the mark with deionized water and mixed. Then 25 ml of this solution is pipetted in the flask into a 400-ml beaker and deionixed water added to about the 200-ml mark of this beaker. As

before, 5 ml of concentrated sulfuric acid, 5 ml of concentrated phosphoric acid, a stirring bar, and five drops of the redox indicator are added to the beaker. The redox titrant is titrated to a green endpoint recording the amount of titrant dispensed.

Preparation of a chromium plating sample solution for total chromium analysis by redox titration requires that 10 ml of sample solution is pipetted into a 500-ml volumetric flask filled to the mark with deionized water and mixed. Then 25 ml of this solution is pipetted in the flask into a 400-ml beaker and deionixed water added to about the 200-ml mark of this beaker. As before, 5 ml of concentrated sulfuric acid and 5 ml of concentrated phosphoric acid are added to the beaker. In addition, 0.05 ± 0.01 grams of manganese sulfate (a grain), 3.0 ± 0.1 grams of ammonium persulfate, 5 ml of the reagent grade silver nitrate solution, and a stirring rod are added to the 400-ml beaker. This solution is boiled until a steady red color occurs, and then 5 ml of concentrated hydrochloric acid is added, making the solution in this beaker turn yellow. This solution is boiled again until it is clear, with the exception of the silver chloride precipitate, and then the solution is cooled to room temperature. Finally, a stirring bar and five drops of the redox indicator are added to this solution and titrated using the redox titrant to a green endpoint recording the amount of titrant dispensed.

All standard and sample solutions are analyzed in triplicate. Trivalent chromium ion concentrations in the samples are determined by the difference between hexavalent chromium and total chromium and are calculated by simple proportion.

RESULTS AND DISCUSSION

The method presented is actually a method for the chemical analysis of hexavalent chromium and has been adapted for trivalent chromium. Since trivalent chromium is the difference between total chromium and hexavalent chromium, it is possible to measure hexavalent chromium before and after (total chromium) trivalent chromium oxidation for the same solution. The oxidation reaction of trivalent chromium to hexavalent chromium is

$$Cr(III) + (NH_4)^2(S_2O_8) \text{ <--> } Cr(VI) \quad (1)$$

Experimental redox titration data are presented in Table 1 for the potassium dichromate standard solution and in Table 2 for the hexavalent chromium (unoxidized sample) and total chromium (oxidized sample) solutions. The redox titration consists of the following equation:

$$(Cr_2O_7)^{2-} + 6\ Fe(II) + 14\ H^+ \text{ <--> } 2\ Cr(III) + 6\ Fe(III) + 7\ H_2O \quad (2)$$

All hexavalent chromium is in the dichromate form due to the addition of sulfuric and phosphoric acids added to the standard and sample solutions above.

Theoretically, from Eq. (2), it is calculated that a 21.77-ml volume of the titrant at the endpoint is required for the standard solution, which is the value experimentally obtained in Table 1.

Although all standards and samples are analyzed in their dichromate form, all samples are actually in the chromate form and are reported as chromium trioxide using the following two equations for conversion:

$$(Cr_2O_7)^{2-} + 2(OH)^- \text{ <--> } 2(CrO_4)^{2-} + H_2O \quad (3)$$

$$(CrO_4)^{2-} + 2(H)^+ \text{ <--> } CrO_3 + H_2O \quad (4)$$

From Eqs. (3) and (4), it is found that the sodium dichromate standard solution has the equivalent of 245 g/l potassium dichromate or 166.55 g/l chromium trioxide (CrO_3).

Therefore, by simple proportion, the calculation for determining the concentration of chromium trioxide in the sample solution before and after oxidation is

$$g/l\ CrO_3 = (166.55)\ (\text{titrant ratio}) \quad (5)$$

where the titrant ratio is the milliliter of sample titrant used divided by the milliliter of standard titrant used.

From Eq. (5), the values of 251.2 and 261.9 g/l chromium trioxide are respectively calculated for the unoxidized (hexavalent chromium) and oxidized (total chromium) solution data given in Table 2.

The trivalent chromium concentration in Table 2 is 5.6 g/l and is calculated by the following equation:

$$g/l\ Cr(III) = (0.5200)\ (\text{titration term}) \quad (6)$$

where the titration term equals the volume (ml) to titrate the oxidized solution minus the volume (ml) to titrate the unoxidized solution.

It is useful to evaluate the variations in precision for the materials and methods used. Tables 3 through 7 present these data for the 25-ml class-A pipets, 10-ml class-A pipets, 500-ml class-A volumetric flasks, 50-ml class-A burets, and the 4.90-g/l potassium dichromate standard solution, respectively.

The data obtained by this method are sufficient to adequately monitor the trivalent chromium in the chromium plating process providing efficient use of resources. The optimum operating range of trivalent chromium is 0 to 7.5 g/l and the resulting precisions are in the 0 to 1.5-g/l range, providing adequate monitoring of these plating solutions supported by five years of testing.

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TABLE 1. EXPERIMENTAL REDOX TITRATION DATA FOR THE POTASSIUM DICHROMATE STANDARD SOLUTION

Replicate	Titrant Used (ml)
1	21.80
2	21.75
3	21.75
X(avg)	21.77

TABLE 2. EXPERIMENTAL REDOX TITRATION DATA FOR THE CHROMIUM SAMPLE SOLUTIONS

Replicate	Unoxidized Sample Titrant Used (ml)	Oxidized Sample Titrant Used (ml)
1	32.80	34.25
2	32.85	34.25
3	32.85	34.20
X(avg)	32.83	34.23

TABLE 3. PRECISION OF A 25-ml CLASS-A PIPET

Replicate	Volume (ml)*
1	25.04
2	24.99
3	24.96
4	25.03
5	25.01
6	25.05
X(avg)	25.01
Sn	0.03

*Volumes are calculated from the weight-volume relationship of a pipetted deionized water solution corrected for temperature.

TABLE 4. PRECISION OF A 10-ml CLASS-A PIPET

Replicate	Volume (ml)*
1	10.03
2	10.00
3	9.98
4	9.99
5	9.98
6	10.04
X(avg)	10.00
Sn	0.02

*Volumes are calculated from the weight-volume relationship of a pipetted deionized water solution corrected for temperature.

TABLE 5. PRECISION OF A 500-ml CLASS-A VOLUMETRIC FLASK

Replicate	Volume (ml)*
1	500.6
2	500.1
3	499.8
4	500.0
5	500.5
6	499.3
X(avg)	500.1
Sn	0.4

*Volumes are calculated from the weight-volume relationship of the contained deionized water solution corrected for temperature.

TABLE 6. PRECISION OF A 50-ml CLASS-A BURET

Replicate	Volume (ml)*
1	24.94
2	24.98
3	25.02
4	25.05
5	24.98
6	25.05
X(avg)	25.00
Sn	0.04

*Volumes are calculated from the weight-volume relationship of a contained deionized water solution corrected for temperature.

TABLE 7. PRECISION OF A 4.90-g/l POTASSIUM DICHROMATE STANDARD SOLUTION BY TITRATION

Replicate	$K_2Cr_2O_7$ Conc. (g/l)*
1	4.91
2	4.88
3	4.90
4	4.89
5	4.91
6	4.91
X(avg)	4.90
Sn	0.01

*Potassium dichromate as chromic acid concentrations are calculated using Federal Specification O-C-303D which is a standard chemical analysis method for chromic acid.

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